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Net Density of Ramie Cellulose

By

Usaburo Yoshida and **Bunsuke Takei**

(Received November 10, 1931)

Abstract

A method of measuring the densities of fibrous, powdery and porous substances, which are liable to occlude gases and water, is described. With this method the density of retted ramie-fibre is observed to be 1.622, and those of purified and mercerized ramie cellulose are observed to be 1.614 and 1.610 respectively. These are the greatest values observed hitherto.

In a paper[1] recently published, one of the writers and N. Matsumoto suggested that the net density of cellulose was probably somewhat higher than the values hitherto observed. Since then, the writers have attempted to get more accurate values of the densities of retted ramie fibre, purified and mercerized ramie cellulose. The method and the results of the measurements are described below.

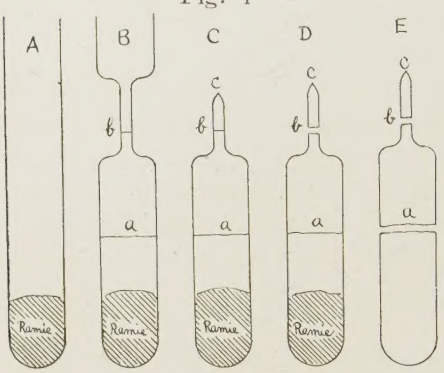
The point, to which most attention must be paid in this kind of measurement, is how to take off the gas and the water which are occluded in the specimen. This was simply done by heating and evacuating properly the glass tube containing the specimen. The procedure of the experiment is illustrated in Fig. 1.

A certain quantity of the specimen, which had been kept in a desiccator, was weighed with a balance, and it was put into a glass tube which had been sealed at one end, as is shown by A in Fig. 1. A part of the tube was necked with a burner several centimeters from its sealed end as is shown by B in the same figure. Sufficient care was taken, of course in this case, not to heat the specimen contained in the sealed end. The tube was scraped with a file at the parts marked *a* and *b* in B, Fig. 1, so as to be easily broken after-

1. U. Yoshida and N. Matsumoto, These Memoirs, **14**, 115 (1931)

wards. Then the tube was connected to an oil rotary pump which was capable of evacuating down to a pressure of about 0.01 mm. of mercury. When the tube was being evacuated, the tube was kept at a proper temperature by being placed in a water or an oil bath. When the evacuation was ended the tube was sealed at its neck as shown in C, Fig. 1. The tube thus sealed was weighed, and then its volume was measured by immersing it in water contained in a measuring cylinder. The volume of the sealed tube thus observed served for the reduction of weighing in vacuo; and the values of those treated in the present experiment were from 7 to 13 c.c. Distilled water was then introduced into the tube by breaking the neck of the tube at *b* in distilled water in the way shown by D in Fig. 1. In this case some small bubbles were usually seen in the tube even when the tube was evacuated thoroughly. These bubbles were not due to imperfect evacuation, but they were confirmed to be caused by the evolution of air which had been absorbed by the water. To avoid as far as possible the formation of the air bubbles, the distilled water was first boiled, cooled as quickly as possible by dipping the vessel containing the boiled water in running water, and then the water thus cooled was introduced into the evacuated glass tube containing the specimen by breaking the neck of the glass tube at the point *b* in the cooled water. Even with this procedure some bubbles of much smaller size were seen to be still formed in the tube. But these small bubbles were observed to disappear entirely on merely leaving the tube in the cooled water for more than about five hours in the present case. This is probably due to the reabsorption of the evolved air into the water. This precaution to eliminate the presence of air bubbles is very important, and it was always taken when accurate determination of the density was wanted.

Fig. 1



Next the weight of the specimen in distilled water was measured. After the weight in distilled water of the glass tube containing the specimen, and the broken neck, both of which were perfectly filled with water, had been measured in the usual way, the glass tube was

broken along the filed line *a*, and the specimen was taken out of the tube. Then the weight in distilled water of all the parts of the broken glass tube, as shown by E in Fig. 1, was measured in the same way, and the weight of the specimen only in distilled water was obtained immediately.

Finally after all the parts of the broken glass tube had been freed from water and well dried, their weight in air was measured. From the weight of the glass tube only and that of the sealed glass tube containing the specimen which was well evacuated, we can obtain immediately the net weight of the specimen. From this net weight of the specimen and its weight in distilled water, the net density of the specimen was calculated.

In the procedure above stated, the reduction of weighings in vacuo and the correction due to the change of the density of water with temperature were, of course, always made.

As preliminary experiments, the writers measured the densities of retted ramie fibre, purified and mercerized ramie cellulose, evacuated for various duration of time by being heated to different temperatures in the bath. The results of the experiments are shown in Figs. 2 and 3. In the case of Fig. 2 the time of evacuation was kept constant at 7 hours, and the temperature of the bath changed from the room temperature to 160°C. This temperature of the bath being taken as abscissa, the densities of retted ramie fibre and cellulose are represented as ordinate in the upper half of Fig. 2; and the reduction of weight of the specimen by evacuation, which is represented in percentage with reference to the original weight of the unevacuated specimen, is taken as ordinate in the lower half of the same figure.

Fig. 2

△ for retted ramie fibre,
× for purified cellulose,
○ for mercerized cellulose

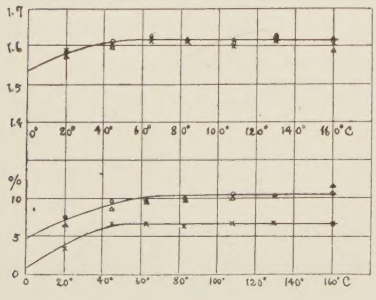
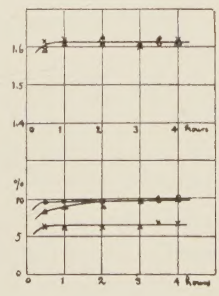


Fig. 3

△ for retted ramie fibre
× for purified cellulose
○ for mercerized cellulose



In the case of Fig. 3 the temperature of the heating bath was kept constant at 70°C, and the time of evacuation changed from 30 minutes to 4 hours. The time of evacuation is taken as abscissa in this case, and the ordinates in the upper and the lower halves have the same meaning respectively as in Fig. 2 From the curves in Figs. 2 and 3, we know that when the specimen is heated at 70°C, the density and the reduction in weight remain unchanged for evacuations of longer than about two hours, and that when the time of evacuation is seven hours, the density and the reduction in weight reach their maximum values and remain constant for heatings higher than about 50°C, so far as the present experiment is concerned. The fact that the density and the reduction in weight attain their maximum values at a certain stage means that at least nearly all the gas and water occluded in the specimen are driven out at this stage. Thus a reliable value for the density will be obtained under the conditions which provide such maximum values of density and reduction in weight; and the value of the density of retted ramie fibre and ramie cellulose, which is taken to be most reliable as will be stated later, was obtained under such conditions.

Here it must be noted that when the specimen is heated to a temperature higher than about 130°C a slight carbonization begins to occur. Thus the heating of the specimen to a temperature higher than this must be avoided when an accurate density is required.

As the experiments shown in the curves in Figs. 2 and 3 were preliminary, the writers did not use much of the specimen, the quantity being usually several decigrams in each experiment.

Table I

Net Density

Retted ramie fibre	Purified ramie cellulose	Mercerized ramie cellulose	Remark
			Evacuated for
1.620	1.612	1.608	7 hours at 77°C
1.621	1.613	1.611	3.5 hours at 75°C
1.624	1.617	1.612	4 hours at 70°C
1.622	1.614	1.610	Mean density

Here it must be remarked that the present experiment was performed under the assumption that the net density of cellulose does not suffer any appreciable change by its swelling in water. If there is any suspicion on this point, it will be safer to measure again the density of cellulose by dipping it into some suitable liquid other than water.

By taking the various precautions stated before, the measurements of the most reliable densities of retted ramie fibre, purified and mercerized ramie cellulose were performed and the results are tabulated in Table I. The quantity of the specimen used in this case was from 0.7 gms. to 1.7 gms.; and the probable error of the measurements was about ± 0.3 per cent. The density of the retted ramie fibre is 1.622, and it is somewhat larger than those of the others. Though the density of the purified ramie cellulose is a little larger in the table than that of the mercerized, the difference is smaller than the limit of experimental error, and consequently they may be looked upon as nearly the same.

So far as the writers are aware, the values of the densities of retted ramie fibre, purified and mercerized ramie cellulose obtained by them are larger than those observed hitherto for cellulose. For example, O. L. Sponsler[1] took 1.57, R. O. Herzog[2] 1.52 and K. R. Andress[3] 1.59 as the density of pure cellulose.

If some small cavities which do not permit the intrusion of water existed in the tissue of the fibre, then the density of the specimen measured would be smaller than the net value even with the method employed by the writers. The presence of such small cavities was examined for microscopically with a specimen soaked with water, which had been well degassed previously by the method mentioned before. But no trace of the presence of such small cavities and of small bubbles on the surface of the specimens could be detected. This result seems to deny the possibility of much greater values for the densities of retted ramie fibre, purified and mercerized ramie cellulose, than those observed by the writers.

It has already been stated that the weight of the specimen decreases with evacuation in parallel with the increase in its density. This seems to be mainly due to the expulsion of water occluded

1. The Journal of General Physiology, **7**, 677 (1926)
2. The Journal of Physical Chemistry, **30**, 457 (1926)
3. Zs. f. phys. Chem., **136**, 279 (1928)

Table II

Retted			Purified			Mercerized			
Density of evacuated ramie	Reduction of weight by evacuation in %	Density of unevacuated ramie (calc.)	Density of evacuated ramie	Reduction of weight by evacuation in %	Density of unevacuated ramie (calc.)	Density of evacuated ramie	Reduction of weight by evacuation in %	Density of unevacuated ramie (calc.)	
1.618	9.85	1.524	1.606	6.5	1.545	1.611	9.84	1.520	
1.612	10.06	1.517	1.594	6.64	1.535	1.606	10.41	1.512	
1.626	10.15	1.530	1.610	6.62	1.546	1.614	10.25	1.518	
1.616	10.00	1.521	1.606	6.01	1.548	1.617	9.88	1.523	
1.608	8.80	1.526	1.614	6.25	1.553	1.610	9.83	1.518	
1.622	8.83	1.537	1.608	6.12	1.550	1.607	9.04	1.523	
1.592	8.26	1.516	1.613	6.28	1.553	1.603	9.46	1.516	
1.540	3.67	1.511	1.587	3.34	1.556	1.558	5.59	1.512	
1.533	3.74	1.503	1.573	3.42	1.544	1.553	5.54	1.506	
		1.521			1.548			1.516	Mean value
		1.528			1.541			1.511	observed by using freezing mixture
		1.47			1.544			1.507	Direct observ.

in the specimen, because the colour of the electric discharge through a Geissler tube, connected in parallel with the glass tube containing the specimen, is the same as that peculiar to hydrogen gas. Thus by assuming that the reduction in weight by evacuation is entirely due to the extraction of liquid water adhering to the specimen, the writers calculated the densities of the unevacuated specimens, and they are given in the third, sixth and ninth columns in Table II respectively for the retted ramie fibre, and purified and mercerized ramie cellulose. The values thus calculated are nearly the same respectively for each one of the three kinds of the specimens. The mean values for the three different kinds of specimens are given in the third horizontal row from the bottom in Table II. The values given in the second horizontal row from the bottom are obtained by evacuating the specimens for about 30 minutes by cooling them in a freezing mixture, so as to prevent the extraction of liquid water from the specimens as far as possible. The agreement between the values given in the third and the second horizontal rows from the bottom of the table seems to be almost satisfactory for the three different kinds of specimens respectively. This seems to justify our previous assumption that the

reduction of weight of the specimen by evacuation is mainly due to the expulsion of liquid water adhering to the specimen. The values of the densities given in the horizontal row at the bottom of the table are those measured in the usual way without any evacuation. The values for the purified and mercerized cellulose are in fair agreement with those obtained with evacuation by cooling the specimens with freezing mixture. However the value for the retted ramie fibre is much smaller than that obtained with evacuation by cooling with freezing mixture. This is caused by the presence of very small air bubbles adhering tightly to the ramie fibre when it is immersed in water. Thus the value of the density, 1.47, for the retted ramie fibre is entirely erroneous.

It seems to be not unprofitable to mention that the reduction in weight by evacuation is nearly the same for the retted ramie fibre and the mercerized ramie cellulose, and that that for the purified ramie cellulose is much smaller than those for the former two. The value for the former two is 10% and that for the latter is 6.5% of the original weight when the specimens are thoroughly evacuated. This shows that the purified ramie cellulose is less hygroscopic than the other two.

Table III

Reduction of weight in % refering to the original weight

	Retted ramie fibre	Purified ramie cellulose	Mercerized ramie cellulose
Dried in desiccator	1.81	1.36	1.84
Evacuated thoroughly	9.87	6.88	10.76

After all the experiments described above had been finished, the writers found that the exsiccant in the desiccator which had been used to dry the specimens had become very dull, and that the weight of the specimen was the same regardless of whether it was kept in the desiccator or left in free air. Thus the old exsiccant was replaced by a new one, and the specimens were kept in the desiccator filled with the new exsiccant for several days. During this time the specimens were weighed occasionally, and their weights were seen to diminish gradually till they reached some stationary value after about two days. The reduction in weight at this stationary state, which is

expressed in percentage with reference to the original weight, is given in the second horizontal row of Table III. The reduction in weight is nearly the same for the retted ramie fibre and the mercerized ramie cellulose, and that for the purified cellulose is smaller than that for the former two, in accordance with the fact observed before. The reduction in weight of the specimens when they are thoroughly evacuated is given in the horizontal row at the bottom of the same table.

Here it must be noted that the method described above for measuring the density accurately, can be well applied to any substances, such as powdery, fibrous or porous substances, which are liable to occlude gases and water.

In conclusion, the writers wish to express their sincere thanks to Prof. G. Kita of the department of industrial chemistry for his kindness in giving various suggestions and also in furnishing all the test materials to the writers. They wish also to express their hearty thanks to Prof. K. Koriba of the botanical department for the interest he has taken in the research, and also to Mr. H. Komuro for his kindness in examining the specimens with the microscope.

On the Arrangements of the Micro-crystals in Copper and Gold deposited by Electrolysis

By

Hideki Hirata and Yoshio Tanaka

(Received November 12, 1931)

Abstract

The arrangements of the micro-crystals in electrolysed specimens of copper and gold deposited under various conditions, were examined with X-rays, by the so-called "transmission method". The experimental results thus obtained were found to agree well with those obtained by other experimenters in many respects. But in some respects, especially with regard to the direction of the growth of the deposited copper and that of the largest face of the specimen, some slight modifications are found to be needed in the conclusions arrived at up to the present time.

Introductions

Several X-ray examinations of the crystalline structures of various electro-deposited metals have already been made. But to arrive at a harmonious conclusion, more experimental data are needed even with respect to metals of such simple and well known crystal forms as those belonging to the copper group.

The writers were therefore induced, by way of continuing the investigation carried out in this laboratory with electro-deposited silver,[1] to repeat the experiments with electro-deposited copper. Supplementary to these copper specimens, some specimens of electro-deposited gold were also examined.

It is well known that the crystal forms of these two metals, like that of silver, belong to the face centred cubic system, the length of the edge of a unit cell being respectively 3.60 Å and 4.06 Å in the cases of copper and gold.

1. H. Hirata and H. Komatsubara: These Memoirs, A, **10**, 95 (1926).

Just as in the case of the former one, the present research has been carried out by the so-called "transmission method", the heterogeneous X-rays emitted from the molybdenum anticathode of a Coolidge X-ray tube being utilized. To take the diffraction figures, the photographic plates were always placed perpendicularly to the incident beam at a distance of 3.2–3.5 cms. behind the specimen.

The experimental results thus obtained were found to be slightly different from those previously given by Glocker and Kaupp,[1] Bozorth[2] and others. In the following pages, the parts of the present experimental results which are inconsistent with those of the others, will mainly be dealt with.

Experimental Results

I. Copper.

(i) On the Formation of Irregular Arrangements: The present investigation was first performed with electrolytic copper specimens, deposited from copper sulphate solutions of various concentrations (0.5–1N.) with various current densities (0.07–0.035 amp./cm.^{2}). To obtain these specimens, a cast plate of copper, 7 cms. × 3 cms. in area, was used as anode. Parallel to this anode, a sheet of commercial electrolytic copper of the same size was suspended as the cathode.

The specimens thus deposited usually appeared in a botryoidal form of varying size (0.7–1.2 mm. in diameter). As a result of X-ray investigation, all the specimens belonging to this category were found to give rise to diffraction figures consisting of a number of Debye-Hull rings. This is in no way different from the experimental results given by Bozorth and Takeyama,[3] who suggest that the copper crystal has no marked tendency to be deposited electrolytically with any regularity.

(ii) On the Formation of Fibrous Structures: Next, the writers extended their investigation to other electrolytic copper specimens prepared at the Hidachi Factory of the Kuhara Mining Company. The conditions under which these specimens were prepared are given below:

Electrolyte: 4% Cu, 10% SO_3, and 86% H_2O (in gr. %).

1. Z. S. f. Phys., **24**, 121 (1924).
2. Phys. Rev., **26**, 390 (1925).
3. These Memoirs, A, **13**, 363 (1928).

Temperature : 37°C.
Potential difference : 0.2 volt.
Current density : 0.017 amp./cm.^{2}

Two vats, each 28 cms. × 21.5 cms. × 25.5 cms. in size, were so arranged that the electrolyte was flowing from one vat to the other at the rate of 100 c.c. per minute. A cast plate of copper 1 cm. in thickness was used as the anode. On both sides of this anode, two parallel sheets of copper 16.5 cms. × 19.5 cms. in area, were placed at a distance of 4.5 cms., as the cathodes. The concentration of the electrolyte was kept unchanged while the electrolysis proceeded by adding now and then as much water as was lost by evaporation.

As a result of the electrolysis above mentioned, the copper specimens appeared after 140 hours, in prismatic or pyramidal forms (1.5–3.5 mms. in diameter) with ragged surfaces. It is to be noted that some of the prismatic or pyramidal axes of these specimens were found to be normal to the surface of the cathode, while many others inclined obliquely to this surface. The macro-structure of the pyramidal one is reproduced in Fig. 9, Plate I.

With one of these specimens thus deposited, it was impossible to get any reliable diffraction figure. Not only would its great thickness considerably reduce the intensity of the diffracted rays, but its detachment from the cathode surface might also cause some mechanical distortions in the crystalline structure at the cut end of the specimen. It seemed, therefore, to be of fundamental importance to make the specimens such that they could be utilized in these experiments.

For this purpose, the writers were obliged to remove the outer portion of each specimen by pickling it in dilute nitric acid, before it was examined. When the specimen was pickled until it was reduced to a suitable size, a number of faces made their appearance on this specimen. Of these faces of the specimen thus formed, it was noticed that the largest one was situated nearly parallel to the direction of the prismatic or pyramidal axis, which usually remains unaltered during the process of etching.

By placing this largest face of the specimen perpendicularly to the direction of the incident X-ray beam, we usually obtained a diffraction figure in which the radiating bands predominated, as shown in Fig. 11, Plate I. To obtain this figure, Fig. 11, Plate I, the photographic plate was placed 3.2 cms. behind the specimen. This predomination of the radiating bands in the figure shows us without doubt,

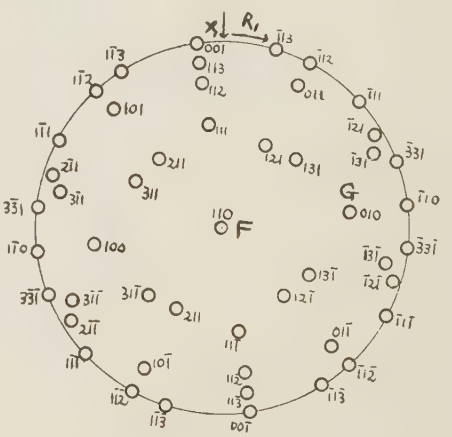
that the copper specimens under examination are mostly of the fibrous structure, as was asserted by Glocker and Kaupp.[1]

As can be seen in Fig. 11, Plate I, all the radiating bands of a diffraction pattern obtained by the procedure above mentioned, are nearly straight in the vicinity of the central spot. This indicates that the axis of the fibre is nearly perpendicular to the direction of the incident beam, and is in a direction nearly parallel to the largest face of the specimen.

Having thus assertained these facts, the writers tried to determine the direction of the fibrous axis in some of the specimens under consideration. This determination could similarly be done as performed by S. Tsuboi[2] to find out the direction of the fibres in silver deposited by the difference of electrolytic solutional pressure.

In the annexed figure, Fig. 1, the normals of various atomic planes of the copper crystal are projected, by taking one of its rhombododecahedral faces 110 parallel to the plane of the paper. This projection was not made by the ordinary method adopted in the crystallographical considerations, but is the orthogonal projection of the pole figure of the copper crystal on the equatorial plane 110, as the latter seems to be more convenient for our further consideration.

Fig. 1



Now, let us provisionary suppose that the incident X-ray beam was made to strike this copper crystal perpendicularly to its $<110>$ axis, taking the direction nearly normal to the 001 face. Then, if the copper crystal is rotated from its initial orientation above mentioned around the $<110>$ axis by a certain angle, a diffraction figure as can be obtained by the normal incidence of the X-ray beam to the axis of rotation is expected to be produced: i. e., the diffraction figure

1. Loc. cit.
2. These Memoirs, A, **11**, 271 (1928).

obtained should consist of a number of radiating bands nearly straight in the vicinity of the central spot.

By the aid of an improved Yoshida's crystallographic globe,[1] we can easily determine the position of each one of these radiating bands above stated. The curves in the annexed figure, Fig. 2, represent diagrammatically the theoretical positions of the prominent radiating bands expected to be produced on the photographic plate placed 3.2 cms. behind the specimen; and the short lines crossing these radiating bands express the calculated positions of the impression of the K_α line of Mo on the same plate.

To draw these curves in Fig. 2, we assumed that the copper crystal was rotated by some 19° around the <110> axis from its initial orientation above mentioned. The projection of this axis of the rotation <110> on Fig. 2 is represented by an arrow F, while the arrow X_1 and R_1 in Fig. 1 represent the direction of the incident beam in the initial orientation of the crystal, and that of the rotation of this crystal respectively.

If we place the original photograph[2] of Fig. 11, Plate I upon Fig. 2, in such a way that the direction represented by F and the centre of the central spot in both figures coincide with each other, a fine agreement between the two figures will easily be observed. This shows us that the orientation of each micro-crystal in the specimen giving rise to Fig. 11, Plate I can be realized by the above stated rotation of a copper crystal. Thus, it seems to be legitimate to consider that the micro-crystals are arranged in a fibrous structure, having one of the [110] axes in common; and the rotation of the micro-crystals around this common axis is about 19° from the initial orientation above mentioned. Moreover, from the indices of the atomic planes attributed to the corresponding theoretical curves in Fig. 2, the radiating bands represented by the symbols I, II, III, IV, V, VI and VII in Fig. 11, Plate I, were also found to be produced by the reflections of the atomic planes belonging to the families (111), (110), (100), (211), (311), (210) and (331) respectively.

Next, to confirm the above considerations still further, the writers investigated the interference phenomena due to the oblique incidences

1. U. Yoshida: Japanese J. Phys., 133 (1927), and S. Takeyama: These Memoirs, A, **11**, 467 (1928).

2. It is to be noticed that the diffraction patterns reproduced in Plate I and II, are interchanged from right to left as compared with those of the original plate.

of the X-ray beam from several directions to the largest face of the same specimen as was used in the case of Fig. 11, Plate I. Fig. 12, Plate I is the diffraction figure taken when the axis of the fibre was tilted 20° from its vertical position towards the incident ray. To take this diffraction figure, the photographic plate was placed 3.4 cms. behind the specimen.

In the annexed figure, Fig. 3, the theoretical positions of the prominent radiating bands expected to appear in the present case, are represented by the full lines: While the shaded part of the same figure is the copy of the diffraction pattern in the original plate of Fig. 12, Plate I. As may be seen from Fig. 3, the agreement between the calculated curves and the observed ones is satisfactory.

Fig. 2

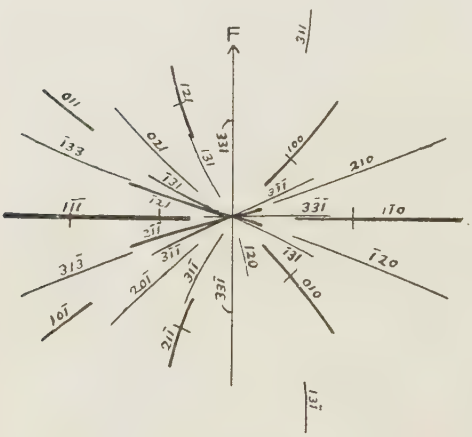
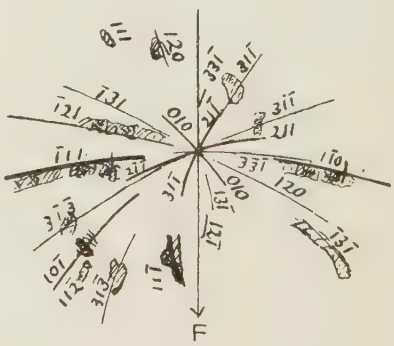


Fig. 3



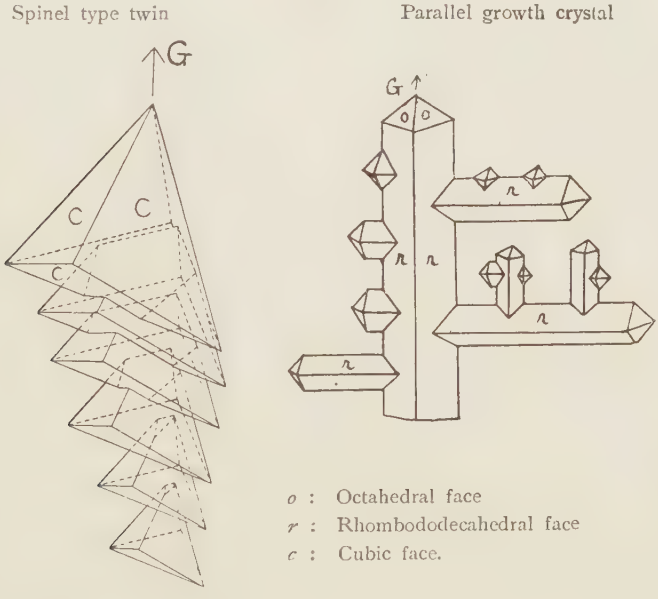
Such an agreement between two curves above mentioned was also found even in the other orientations of the largest surface of the specimen to the incident X-ray beam. Accordingly, our foregoing considerations are again confirmed, and we may conclude that the specimen giving rise to Fig. 11, Plate I has a fibrous structure, the common axis of which coincides with one of the [110] axes, and is situated in the plane of the largest face of this specimen. The direction of the maximum growth, which coincides with the pyramidal axis of the specimen, was found to make an angle of 45° with the direction of this common axis. Thus, the micro-crystal in its initial orientation is seen to be situated with one of the [100] axes in the direction nearly normal to the largest face, and another [100] axis (represented by

G in Fig. 1) in the direction parallel to the maximum growth of the specimen.

Not only the diffraction figure reproduced in Figs. 11 and 12, Plate I, but those obtained with other specimens belonging to this category were also found to be explainable by considerations similar to the above. This shows us that these specimens are of the crystalline structure nearly the same as that of the so-called " parallel growth " copper crystals (see Fig. 4); the difference between two structures above mentiond is only due to the rotation of the micro-crystals in these specimens having one of the [110] axes in common.

Here it must be remarked that the above statement is rather a general one obtained from several specimens. Here and there occasionally a few exceptions were detected: e. g., Fig. 13, Plate I, obtained

Fig. 4



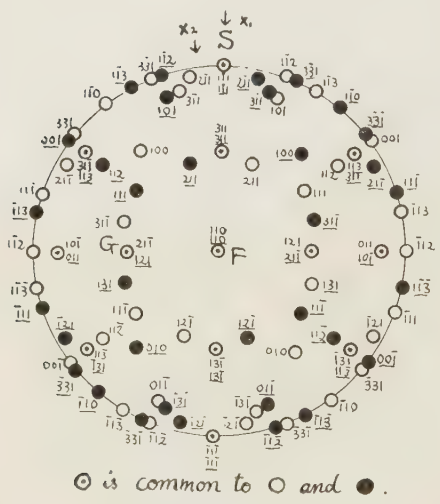
o : Octahedral face
r : Rhombododecahedral face
c : Cubic face.

with a specimen belonging to this category, was found not to be explainable by the foregoing considerations. To take this diffraction figure, Fig. 13, Plate I, the photographic plate was placed 3.5 cms. behind the specimen.

Now, let us advance our arguments with respect to the crystalline structures of the specimens giving rise to a diffraction figure such as that reproduced in Fig. 13, Plate I.

If we suppose that two copper crystals are so situated as to form a so-called "spinel type twin" (see Fig. 4), then the orthogonal projection of these two crystals corresponding to Fig. 1 should be represented as in the annexed figure, Fig. 5. To distinguish the atomic planes of one of these crystals from those of the other, their points of projection are expressed in Fig. 5 by the white circles, and those corresponding to the other by the black ones. The points S and G in Fig. 5, are the projections of the directions represented by the same letters in Fig. 4, which coincide respectively with the normal of the flat surface and the direction of the maximum growth of the spinel twin. As can be seen in Fig. 5, the one set of points of projection expressed by the white circles is distributed in identically the same manner as in Fig. 1, while the other given by the black ones is the same as obtained on rotating Fig. 1, through an angle 180° around the direction S.

Fig. 5



Now, let us suppose that the micro-crystals in the specimens have two ideal orientations as is suggested by the two sets of points in Fig. 5; then the radiating bands, as can be seen in Fig. 13, Plate I, are given rise to by the rotations of the micro-crystals around one of the [110] axes, represented by F, in the vicinities of the two ideal orientations above mentioned. Here it may be noticed that in each one of these two ideal orientations, the micro-crystal has one of its [111] axes in the direction normal to the largest face of the specimen, and one of its [211] axes in the direction parallel to the maximum growth.

As a consequence of the foregoing supposition, Fig. 13, Plate I can be considered to be a superposition of two figures, the one being given rise to by a set of atomic planes corresponding to the white circles in Fig. 5, and the other, by those corresponding to the black ones. By calculation, it was found that the former set of atomic

planes gives rise to a diffraction figure as shown in Fig. 6a; while the latter is responsible for the formation of Fig. 6b. To draw these two figures, the angles of rotations of the micro-crystals were taken as 11° and 28° respectively in the cases of Figs. 6a and 6b from two initial orientations, and a micro-crystal in its initial orientations corresponding to Figs. 6a and 6b, was considered to be so situated that the directions represented respectively by the arrows X_1 and X_2 in Fig. 5, coincided with the direction of the incident X-ray beam.

Fig. 6

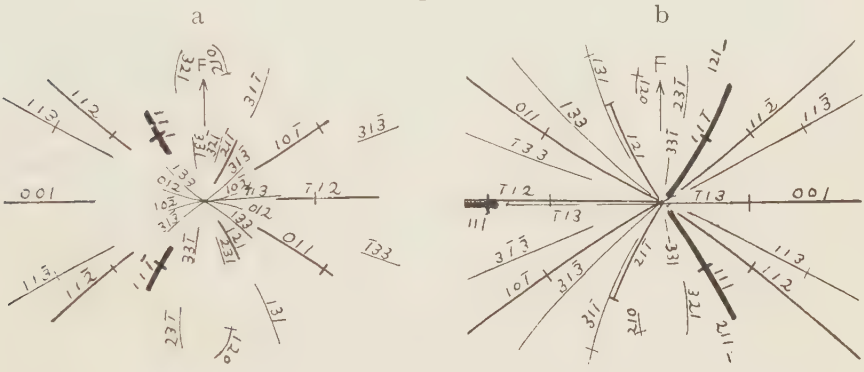
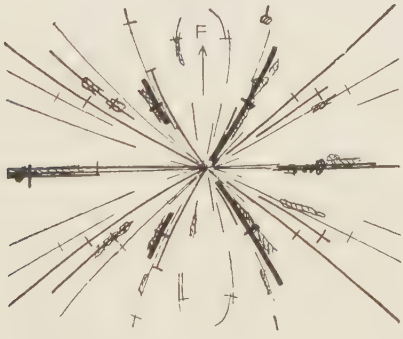


Fig. 7



This being confirmed, it is presumable that the general features of Fig. 13, Plate I must be in fine accordance with the theoretical curves obtained by combining Fig. 6a and 6b. In the annexed figure, Fig. 7, the combination of these two figures above mentioned is represented by the full lines, while the part represented by the shadow in the same figure is a copy of the diffraction pattern in the original plate of Fig. 13, Plate I. As may be seen from Fig. 7, the agree-

ment between the calculated curves and the observed ones is rather satisfactory.

Accordingly, our foregoing suppositions were confirmed as correct and we may consider that the specimen giving rise to Fig. 13, Plate I is of a fibrous structure, the common axis of which is also [110] as in the former case. Furthermore, it was found that the micro-crystals in the specimen were rotated by a small angle from a certain orientation, in which one of the (111) planes of the copper crystal is placed roughly parallel to the largest face, and one of the [211] axes lies nearly parallel to the direction of the maximum growth of the deposited copper. In short, Fig. 13, Plate I may be said to be produced by the rotations of two copper crystals so situated in relation to each other as to form a spinel type twin, around one of their [110] axes.

From our foregoing argument in connection with the specimens of fibrous structure, we arrive at the following conclusions :—

(1) The specimens under consideration consist of micro-crystals arranged in such a way that the common axis is one of the [110] axes of the copper crystal.

(2) For the majority of these specimens, the micro-crystals are rotated within a certain angle around the common axis from the initial orientation, in which one of the (100) planes of the copper crystal is situated nearly parallel to the largest face of the specimen. As the common axis makes an angle 45° with the direction of the maximum growth of the specimen, this direction of the growth is nearly parallel to the normal of another (100) plane of the micro-crystal in the initial orientation.

(3) Some of the specimens consist of micro-crystals rotated around the common axis above stated from two initial orientations. Each of these two initial orientations has one of the [111] axes in the direction parallel to the normal of the largest face of the specimen, and one of the [211] axes in the direction of the maximum growth.

The above conclusions agree well with those previously given by Glocker and Kaupp, excepting the point that one of the [100] or [211] axes, instead of the fibrous direction [110] in the previous experiments, lies roughly parallel to the direction of the specimens in the present experiments.

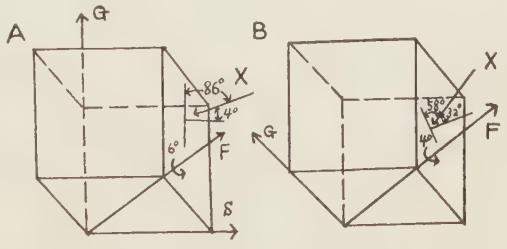
(iii) On the Formation of Single Crystals: A crystalline structure resembling more closely that of the parallel growth crystal of copper,

was observed in some of the specimens which appeared mixed with the fibrous ones, as a result of the process of electrolysis previously mentioned. The diffraction patterns obtained with these specimens, as is shown in Figs. 14 and 15, Plate II, consist of a number of somewhat elongated Laue's spots. To take these two figures, the specimen was so placed at a distance of 3.2 cms. in front of the photographic plate, so that the direction of its maximum growth became parallel to the direction represented by the arrow G on the photographic plate.

From the distributions of Laue's spots, it was found on the one hand, by making use of the Yoshida's globe, that the former figure, Fig. 14, Plate I, can be produced when the direction of the incident X-ray beam is inclined 90°, 4° and 86° respectively to the normal to the atomic planes 100, 010, 001 of a single-crystal of copper; while on the other hand, when the direction of the incident beam is inclined 32°, 19° and 84° respectively to the normals to the atomic planes 010, 011 and 100 of a single crystal, was confirmed by the distribution of Laue's spots to agree well with that of the latter figure, Fig. 15, Plate I. Moreover, the directions represented by the arrows G in these two figures, Figs. 14 and 15, Plate I, were found to coincide respectively with the normals to the atomic planes 001 and 100 within the limits of experimental error.

If we represent diagramatically the orientations of the copper crystal giving rise to Figs. 14 and 15, Plate II, the figures shown in A and B, Fig. 8, may respectively be obtained from the above considerations. It is noticed that in the orientation represented by A, the incident X-ray beam takes the direction nearly parallel to the normal of the 010 plane: But in B, the direction of the incident X-ray beam is inclined obliquely to any one of the prominent atomic planes of the copper crystal. This fact is due to the lack of the largest face of the specimen giving rise to Fig. 15, Plate II.

Fig. 8



X. Direction of the incident X-ray beam.
F. Direction of the fibrous axis.
G. Direction of the maximum growth of the specimen.
S. Direction normal to the largest face of the specimen.

From our arguments with respect to the specimens under con-

sideration, we may conclude that each one of these specimens is mostly made up of a single crystal of copper, having one of its [100] axes in the direction of the maximum growth of the deposited copper, and another [100] axis normal to the largest face (if there is any). In short, the crystalline structure of the specimens giving rise to Figs. 14 and 15, Plate II, is the same as that of the parallel growth copper crystal.

Hitherto, we have treated the diffraction patterns in Figs. 14 and 15, Plate II as ordinary Laue's figures. But strictly speaking they are not exactly so; and a slight elongation of each Laue's spot indicates the presence of a fibrous nature of weak degree. By calculation, it was found that one of the [110] axes in the specimens was also arranged parallel to the direction of the fibre, and the angle of rotation of the micro-crystals around this direction was respectively 6° and 4° in the cases of Figs. 14 and 15, Plate II.

II. Gold

The gold specimens mainly used in the present experiment were gold foils electrolytically deposited on sheets of copper, silver and gold at the laboratory of the Imperial Mint Osaka. Supplementary to these, a specimen of a spongy form prepared at the Mint was also examined.

We are not informed of the procedure adopted in the electrolysis at the Mint, excepting with regard to the specimen of spongy form. The conditions under which this spongy specimen was prepared are given below:

Electrolyte: 140 c.c. saturated water solution of $AuCl_3$, 10 c.c. HCl.
Temperature: 20°C.
Potential difference: 1 volt.
Initial current density: 0.14 amp./cm².

A plate of pure gold 2 mms. in thickness and 3 cms. × 3 cms. in area was used as the anode. Parallel to the anode, a sheet of gold, 0.5 mm. in thickness and 10 mms. × 2 mms. in area, was suspended as the cathode, at a distance of about 3 cms. from the anode. Owing to the increase of the volume of the electro-deposited substance, the current density through the electrolyte was found to increase gradually in the course of the electrolysis. The macro-structure of the spongy specimen thus deposited is reproduced in Fig. 10, Plate I.

Diffraction figures were taken with the electro-deposited gold

foils above mentioned. To take these figures, the specimens were so placed that the foliated surface was perpendicular to the incident X-ray beam.

The diffraction phenomena thus investigated with all the specimens of this category were found to be essentially the same. Each one of these specimens gave rise to a diffraction figure consisting of a number of Debye-Hull rings. This shows us without doubt that the arrangement of the micro-crystals in each specimen has no regularity with regard to the surface of the foil. As an example of these diffraction figures, the one obtained with gold deposited on copper plate is reproduced in Fig. 16, Plate II. To take this diffraction figure, the photographic plate was placed 3.2 cms. behind the specimen.

Next, to ascertain whether any regularity with respect to the other directions might exist or not in these specimens, the writers investigated the diffraction phenemena obtained by rotating some of the specimens under consideration, but no regularity was found; the diffraction figures obtained in this case also consisted of Debye-Hull rings. Accordingly, it was confirmed that the gold foils examined are mostly made up of an irregular aggregation of micro-crystals.

Similar investigations were carried out with the spongy specimen, and it was found that the diffraction figure given rise to by this specimen was also an assemblage of Debye-Hull rings. Thus we may conclude, that the spongy specimens are of the same crystalline structure as the electrolytic gold foils, in which the micro-crystals of gold are arranged without any regularity.

Summary.

The arguments which have hitherto been advanced with respect to electro-deposited copper and gold, lead us to the following conclusions :—

(1) As was already known, the micro-crystals of copper are deposited electrolytically without any regularity under ordinary conditions. But, under certain conditions, the micro-crystals of copper have a tendency to arrange themselves in a fibrous-like manner, having one of the [110] axes in common; and occasionally the rotation of micro-crystals of copper around this common axis is so small that they form a crystalline structure nearly the same as that of a single crystal.

(2) The direction of the maximum growth and that of the normal to the largest face in a quasi-single crystal of copper above stated,

are closely related to those in a "parallel growth" natural crystal. As one of the [100] axes of each micro-crystal in the specimen lies roughly parallel to the normal of the largest face, another [100] axis nearly coincides with the direction of the growth of the deposited copper.

(3) Most of the fibrous specimens of electro-deposited copper are of the crystalline structure nearly the same as that of a "parallel growth" crystal, excepting the presence of a fibrous nature in these specimens due to the small rotation of micro-crystals around their common axis [110]. But, some of these fibrous specimens consist of two groups of micro-crystals rotating around the same common axis as before; a micro-crystal belonging to one of these groups is so situated as to form a "spinel type twin" with another micro-crystal belonging to the other.

(4) The micro-crystals of gold have no marked tendency to deposit themselves with any regularity.

The above conclusions contradict slightly those of Glocker and Kaupp[1], who suggest that the direction of the growth of electro-deposited metals coincides with that of the fibrous axis.

In conclusion, the writers wish to express their best thanks to Professor U. Yoshida and Professor D. Uno for the interest they have taken in the experiments, and to Professor A. Matsubara for his efficacious advice on many occasions. Their thanks are also due to Dr. Y. Kimata of the Hidachi Factory of the Kuhara Mining Company, and to Dr. H. Komatsubara of the Imperial Mint, who kindly supplied many samples required for the present investigations.

Institute of Metallography.
Kyoto Imperial University.

1. Loc. cit.

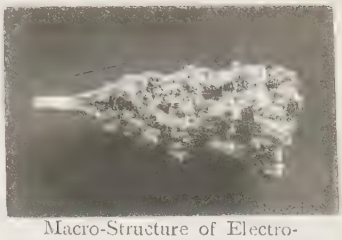
Plate I

Fig. 9

Macro-structure of Electro-deposited Copper

× 19

Fig. 10



Macro-Structure of Electro-deposited Gold

1 : 1

Fig. 11

Copper

Fig. 12

Copper

Fig. 13

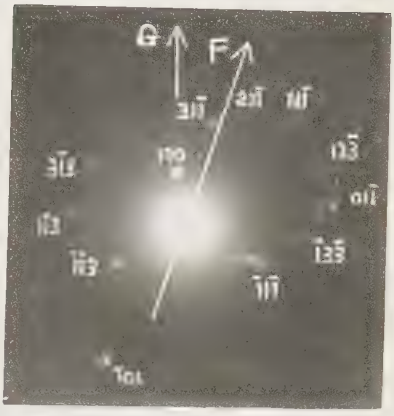
Copper

Plate II

Fig. 14

Copper

Fig. 15



Copper

Fig. 16

Gold

The Arrangement of the Micro-crystals in Compressed Single-crystal Plates of Aluminium, Part IV

By

Yoshio Fukami

(Received November 14, 1931)

Abstract

When rectangular single-crystal plates of aluminium were thoroughly compressed, the manner of the fibrous arrangements of the micro-crystals which were produced by the compression was seen to be divisible into four different types, the axis of the fibrous arrangement being always parallel to the direction of flow of the metal. These four different types occurred according to the initial crystallographic orientation of the specimen, depending mainly on the direction of the longer side of the specimen in reference to the crystallographic axes. In the present investigation, the relation between the initial crystallographic orientation of the specimen and the type of the fibrous arrangement of the micro-crystals produced by thorough compression, was examined closely.

In the previous investigations[1], it was made clear that, when a rectangular single-crystal plate of aluminium was compressed to a thickness of less than about 10% of the initial thickness, the micro-crystals in the specimen took the arrangement of an imcomplete fibre whose fibrous axis was always parallel to the direction of flow of the metal on compression, and that the manner of the fibrous arrangement might be divided into four different types, depending on the initial crystallographic orientation of the crystal mainly with respect to the direction of the longer side of the specimen. We named these four different types of fibrous arrangement (1), (2), (3) and (4), and they are illustrated in Table I. For example, it is shown in type (1) that most of the micro-crystals in a specimen are so arranged by thorough compression that their [111] and [110] axes and their (211) plane are nearly parallel to the direction of flow of the metal, to the direction

1. These Memoirs, **12**, 261 (1929);- **13**, 299(1930);- **14**, 97 (1931)

Table I

Type	Direction of flow of the metal (or fibrous axis)	Direction of the longer side	Plane parallel to the flat surface
(1)	[111]	[110]	(211)
(2)	[211]	[111]	(110)
(3)	[100]	[110]	(110)
(4)	[110]	[100]	(110)

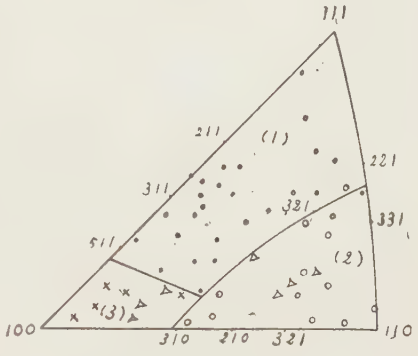
of the longer side and to the flat surface of the specimen respectively. Mutatis mutandis, the same description applies to the other types given in Table I. It was also found that, of these four types, the first two occurred more frequently than the last two; and this fact was explained, at least to some extent, by the possible number of the crystallographic axes present in the cubic crystal of aluminium.

The object of the present investigation is to examine more closely, in continuation of the former investigations, the relation between the initial crystallographic orientation of the specimen and the fibrous arrangement of the micro-crystals produced by thorough compression. The results obtained with 51 specimens, which were compressed to a thickness of about 10% of the initial thickness, are described below. The length of the shorter and the longer side of these rectangular specimens was about 3 mms. and 5 mms. respectively; and the part of the specimen enlarged in breadth by compression was etched carefully off by some dilute acid at each step of the compression, so that the specimen had the same breadth as before. As shown by the third column of Table I, the crystallographic axis which becomes nearly parallel to the longer side of the specimen as a result of compression is any one of the [111], [110] or [100] axes which has initially a slight inclination to the longer side of the specimen. Of such three axes of the initial single crystal of aluminium plate, if the one which becomes nearly parallel to the longer side of the specimen as a result of compression is known, the kind of the fibrous arrangement of the micro-crystals produced by the compression will immediately be known by the aid of the crystallographic globe[1]. Thus special attention was paid in the present investigation to the initial orientation of that crystal axis which became nearly parallel to the direction of the longer side owing to compression.

In Fig. 1 the initial directions of the longer sides of 51 specimens,

1. Japanese J. Phys., **4**, 133 (1927).

Fig. 1

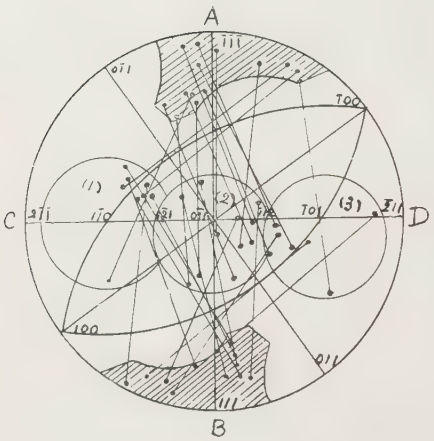


with reference to the crystallographic axes, are shown in stereographic projection. Of these, the ones which correspond to the specimens in which the fibrous arrangement became that in type (2) on thorough compression, are shown by the dots. The ones which correspond to the specimens, in which the fibrous arrangement became that in type (1) on thorough compression are shown by the small circles. Similarly, the small triangles and the crosses correspond respectively to the specimens in which the fibrous arrangements arrived at as a result of compression were types (3) and (4).

In Fig. 1 the writer divided roughly the domain bounded by the margin into three parts: that is, parts (1), (2) and (3). Part (1) contains almost nothing but dots, part (2) contains almost nothing but small circles and some small triangles, and part (3) contains crosses and small triangles. By such division, the dots, the small circles and the crosses are segregated respectively into different parts. But the small triangles are scattered in parts (2) and (3). So far as the present experiment is concerned, a specimen in which the direction of the longer side is in part (1) was observed to belong always to type (2), irrespective of the crystallographic orientation of the normal to the flat surface of the specimen. But in the case of the specimens in which the direction of the longer side is in part (2) or (3), different types of fibrous arrangement were observed, as is shown in Fig. 1, and this fact seems to be made clearer by considering the orientation of the normal to the flat surface with reference to the crystallographic axes. Thus we shall consider the orientation of the micro-crystals in the compressed specimens with reference to the direction of the normal to the flat surface and to that of the longer side of the specimen.

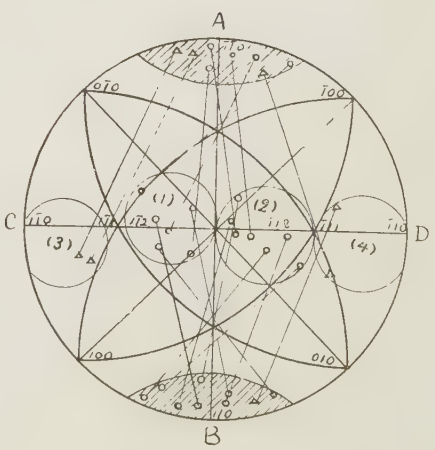
First we shall deal with the specimens which correspond to the dots in part (1) in Fig. 1. A and B in Fig. 2 are the direction of the [111] axis which becomes nearly parallel to the longer side of the specimen as a result of thorough compression; the upper and the lower shaded parts in Fig. 2 correspond to part (1) in Fig. 1 and the dots in these shaded parts also correspond to the dots in part (1)

Fig. 2



in Fig. 1. The dots which are scattered in the neighbourhood of the line CD represent the directions of the normal to the flat surface of those specimens which correspond to the dots in the shaded parts. Where two dots are connected by a straight line, it indicates that they belong to the same specimen. Thus the angle subtended between such two dots is a right angle. The writer divided the dots in the neighbourhood of CD into three groups, namely (1), (2) and (3). On thorough compression, the dots in the upper and lower shaded parts approached respectively A and B, and simultaneously the dots belonging to groups (1), (2) and (3) approached respectively the [1$\bar{1}$0], [0$\bar{1}$1] and [$\bar{1}$01] axes. In other words, in each case, the dodecahedral face became nearly parallel to the flat surface. Therefore, the [211] axis which is perpendicular to the [111] axis, that becomes nearly parallel to the longer side, and which is also perpendicular to the [110] axis that is nearly perpendicular to the flat surface, became nearly parallel to the flow of the metal as a result of compression. For instance, when the [1$\bar{1}$0] axis on CD becomes nearly perpendicular to the flat surface, the [$\bar{1}\bar{1}$2] axis on CD becomes nearly parallel to the flow of the metal owing to compression. The fibrous arrangement type (2) was obtained in such a manner.

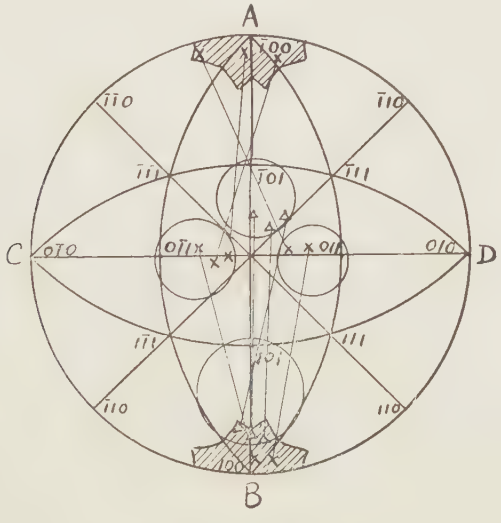
Fig. 3



Next we shall deal with the specimens which correspond to the small circles and the small triangles in part (2) in Fig. 1. In Fig. 3, A and B are the direction of the [110] axis which becomes nearly parallel to the

longer side of the specimen as a result of thorough compression. The upper and the lower shaded parts correspond to part (2) in Fig. 1. The small circles and small triangles in the shaded parts also correspond respectively to the small circles and the small triangles in part (2) in Fig. 1, and show respectively the initial directions of the longer side of these specimens. The small circles and small triangles scattered in the neighbourhood of the line CD represent the direction of the normal to the flat surface of the specimens which correspond to the small circles and the small triangles in the shaded parts respectively. Where the same two marks are connected by a straight line, it shows that they belong to the same specimen. Let us divide the marks in the neighbourhood of CD into four groups, namely (1), (2), (3) and (4). Groups (1) and (2) contain only small circles and groups (3) and (4) contain only small triangles. On thorough compression, the marks in the upper and lower shaded parts approached A and B respectively and the small circles of the groups (1) and (2) approached the $[1\bar{1}2]$ and $[\bar{1}12]$ axes on CD respectively. In other

Fig. 4



words, in both cases the trapezohedral face became nearly parallel to the flat surface of the specimen. Consequently the $[\bar{1}11]$ and $[1\bar{1}1]$ axes on CD which are perpendicular to the $[1\bar{1}2]$ and $[\bar{1}12]$ axes on CD respectively became nearly parallel to the flow of the metal as a result of compression. Thus in the cases of groups (1) and (2), the

fibrous arrangement of type (1) was obtained. In the cases of groups (3) and (4), the small triangles approached to the [1$\bar{1}$0] and [$\bar{1}$10] axes respectively, that is, the dodecahedral face became nearly parallel to the flat surface of the specimen. Therefore the [001] axis on CD became nearly parallel to the flow of the metal as a result of compression. Thus in the cases of groups (3) and (4), the fibrous arrangement of type (3) was obtained.

In Fig. 4, the shaded parts correspond to part (3) in Fig. 1 and the crosses and the small triangles in these parts also correspond to the crosses and the small triangles in part (3) in Fig. 1, and show respectively the directions of the longer side of the specimens. The crosses and the small triangles in the neighbourhood of CD show respectively the directions of the normals to the flat surface of the specimens which correspond to the crosses and the small triangles in the shaded parts. Where the same two marks are connected by a straight line, it indicates that they refer to the same specimen. On thorough compression, the crosses in the upper and lower parts approached A and B respectively. Of the five crosses very near the line CD, the two on the right side of AB approached the [011] axis on CD, and the directions of the flow of the metal approached the [0$\bar{1}$1] axis on CD which is perpendicular to the [011] axis. The three crosses on the left side of AB approached the [0$\bar{1}$1] axis on CD, and the directions of the flow of the metal approached the [011] axis on CD. Thus in the case of the specimens which correspond to the crosses, the fibrous arrangement of type (4) was obtained. On the other hand, the three small triangles in the lower shaded part approached the [101] axis on AB and the three small triangles which are far above the line CD and the crosses, approached the [$\bar{1}$01] axis on AB. Therefore the [010] axis, which is perpendicular to the [101] and [$\bar{1}$01] axes, became parallel to the flow of the metal as a result of compression. The fibrous arrangement type (3) was obtained in such a manner.

The total number of the dots represented in Fig. 1 is 26, which is much larger than that of any of the other marks. The area occupied by part (1) is also much larger than that of any of the other parts. These facts show clearly that the micro-crystals in a thoroughly compressed specimen chiefly tend to take the fibrous arrangement type (2). It was found, in the previous investigation on compressed and rolled pollycrystalline specimens, that the fibrous arrangement of the micro-crystals was the same as type (2); and such fibrous arrangement was also found by S. Tanaka in the case of rolled single-crystal

foils[1]. Moreover, with rolled foils of copper, silver, gold and platinum which belong to the face centred cubic lattice type, the fibrous arrangement of the micro-crystals was observed to be of type (2) by S. Tanaka[2] and Mark and Weissenberg[3].

The number of the small circles and the small triangles in Fig. 1 is 13 and 7 respectively, and the area occupied by part (2) is somewhat large. These facts show that the micro-crystals in a thoroughly compressed specimen have also a somewhat great tendency to take the fibrous arrangement type (1). The same type of fibrous arrangement was also observed by S. Tanaka[4] and Wever[5] in the case of rolled single-crystal foils of aluminium.

The number of the crosses is only 5 in Fig. 1, and the area occupied by part (3) is also very small. These facts indicate that the micro-crystals in a thoroughly compressed specimen have the least tendency to take the fibrous arrangement type (4).

Thus we are now able to determine, at least to some extent, the boundary of the initial crystallographic orientation of a specimen which corresponds to one or other of the four different types of fibrous arrangement described above. Thus if the initial crystallographic orientation of a specimen is known, we can now predict more strictly the kind of the fibrous arrangement of the micro-crystals in a specimen produced by compression.

Finally, when the crystallographic axis which approaches the longer side as a result of compression deviates much initially from being parallel to the latter, the mean orientation of the micro-crystals arranged fibrously as a result of thorough compression also deviates much from the ideal orientation shown in Table I. Thus, when the crystallographic orientation is in the neighbourhood of the boundary, the greater part of the micro-crystals in the specimen seem to take on an orientation intermediate between the different types which correspond to the two parts lying on the two sides of the boundary. In those cases, the writer took three Laue-photographs, by sending the X-ray beam from three different directions: normally to the flat surface, parallel to the flat surface and also to the longer side, and

1. These Memoirs, **10**, 303 (1927)
2. „ **8**, 319 (1925)
3. Zeit. f. Physik, **14**, 328 (1923)
   „ **28**, 69 (1924)
4. These Memoirs, **10**, 303 (1927)
5. Zeit. f. Physik, **28**, 69 (1924)

parallel to the flat surface and also to the direction of flow of the metal on compression. From these photographs he was able with some difficulty to classify such indistinct fibrous arrangements. Figs. 5 and 6, which correspond to type (1) and (2) respectively, are seen

Fig. 5

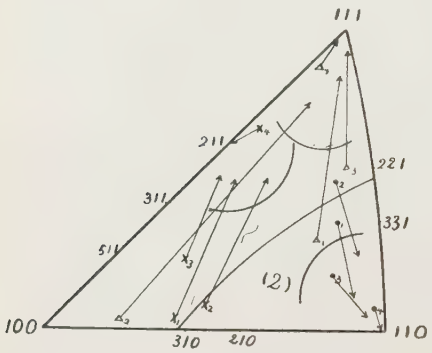
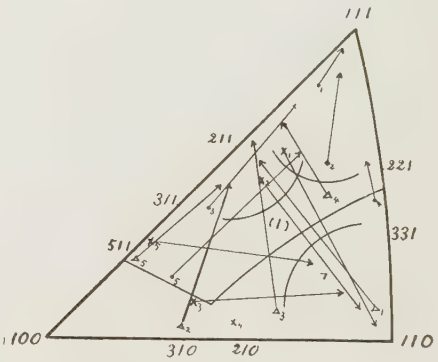


Fig. 6



to illustrate the facts stated above. In these figures, the dots, the small triangles and the crosses show respectively the direction of the longer side, of the flow of the metal and the normal to the flat surface of the specimen at its initial orientation. The numbering of three different marks with the same figure shows that they belong to the same specimen. The ends of the arrows show the positions of the mean crystallographic orientations of the micro-crystals which were scattered at the last compression. Fig. 5 shows that the dots, the small triangles and the crosses approach the [110], [111] and [211] axes respectively as the process of compression is continued, and also shows that the greater the deviation of the initial crystallographic orientation from the ideal orientation, the greater is that of the micro-crystals at the last compression from the ideal orientation. In Fig. 6, the dots, the small triangles and the crosses approach the [111], [211] and [110] axes respectively and we can see the same things in this case as are mentioned in connection with Fig. 5.

In conclusion, the writer wishes to express his sincere thanks to Professor U. Yoshida for his kind guidance and suggestions during this research.

The Arrangement of the Micro-crystals in the Film of Molybdenum obtained by Deposition

By

Takeo Fujiwara

(Received November 20, 1931)

Abstract

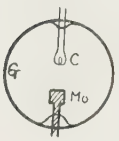
By means of Laue-photographs the arrangement of the micro-crystals in the thin film of molybdenum obtained by deposition was studied. It was found that they are composed of micro-crystals which are so arranged that the (110) plane is almost in the flat surface of the film and a cube edge is nearly parallel to the lengthwise direction, but some of them are composed of somewhat large micro-crystals, which are arranged fibrously with the [110] axis as fibre axis which is normal to the flat surface of the film.

The arrangement of the micro-crystals in deposited metals has already been studied by many investigators; and especially S. Rembinska[1] studied the crystal structure of thin metallic films prepared by cathodic or thermal sputtering by means of a Bragg apparatus. In the present experiment the arrangement of the micro-crystals in molybdenum deposited on a molybdenum anode was examined by means of Laue-photographs.

The deposited molybdenum crystals examined were obtained by the process of heating a molybdenum anode sufficiently by electron bombardement in vacuo so that molybdenum was removed from the anode and was deposited as a thin film on the inner surface of the glass tube in which the anode and cathode were sealed; and then, owing to the increased deposition of the molybdenum on the surface of the glass tube, the deposited film flaked off from it and was deposited reversely on the anode. The apparatus used in this deposi-

1. S. Rembinska: Zeit. f. Phys., **54**, 46 (1929).

Fig. 1



tion is diagrammatically shown in Fig. 1, where Mo is the molybdenum anode, C the hot cathode of tungsten filament and G the spherical glass tube of about 10 cms. in diameter. The potential applied to the tube was about 40 K. V. s., the electronic current passed through 15–20 milliamperes, and the bombardment was carried out for about 200 hours till the deposits came to appear on the anode. Some of the molybdenum deposits thus obtained are shown in Figs. 1 and 2, Plate I, where we can see needle-shaped and dendriform crystals standing perpendicularly to the surface of the anode. In Fig. 3, Plate I, the deposited films which were flaked off from the inner surface of the glass tube, and their traces, are shown.

It was found by a microscopic examination that most of them are thin films composed of the aggregates of the micro-crystals and that some of them are composed of single crystals as shown in Figs. 4, 5, 6 & 7, Plate I, where Figs. 5 & 7 are the enlargements of some parts of the photographs shown in Figs. 4 and 6 respectively.

Then the ordinary Laue-photographs were taken with these crystals by sending a narrow and circular beam of X-rays, which started from the focus on the Mo-target of a Coolidge tube, obliquely to the flat surface of the specimen, the photographic plate being set perpendicularly to the beam of the X-rays. Some of the typical X-ray radiographs thus taken are shown in Figs. 8, 9, & 10 in Plate I, where Figs. 8 & 10 are the Laue-photographs taken with the crystal shown in Fig. 4, Plate I, and Fig. 9, that taken with the crystal shown in Fig. 6, Plate I respectively. In these cases the beam of incident X-rays was made to strike the crystal perpendicularly to its lengthwise direction and obliquely to the normal to its flat surface. In the cases of Figs. 8, 9 & 10, Plate I, the beam of X-rays was inclined to the normal at angles of about 25°, 25° and 10° respectively, and in each figure an arrow indicates the lengthwise direction of the specimen.

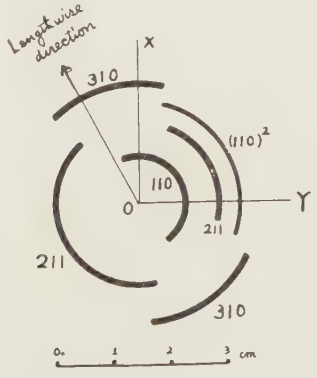
With these radiographs the orientation of the crystallographic axes was determined by treating the Laue-spots with the crystallographic globe.[1] It was found that though the crystal shown in Fig. 6, Plate I, seems to be a single apparently, it is composed of micro-crystals which are so arranged that the $(11\bar{2}0)$ planes are in the flat

1. U. Yoshida: Japanese, J. Phys., **4**, 133 (1927); S. Takeyama: These Memoirs, **12**, 257 (1929).

surface of the crystal and the cube edges nearly parallel to the lengthwise direction, with some scattering around the lengthwise direction. In the crystal shown in Fig. 4, Plate I, the micro-crystals are arranged fibrously with the [110] axis as their fibre axis which is normal to the flat surface.

Thus, I assumed that the [110] axis which is normal to the flat surface is the fibre axis of the micro-crystals and that the beam of incident X-rays strikes the specimen with the inclination of 10 degrees to the normal to the flat surface and perpendicularly to the lengthwise direction, and then I calculated the diagram of the diffraction pattern which might be expected to appear on the photograph. The agreement between the diagram thus calculated and the photograph shows the correctness of the conclusion given above. The calculated diagram Fig. 2, which was drawn by taking 10° as the angle of inclination of the beam of X-rays to the normal to the flat surface of the specimen, corresponds to Fig. 10 in Plate I.

Fig. 2.



In conclusion, I wish to express my sincere thanks to Prof. U. Yoshida, of Kyoto Imperial University for the interest he has taken in this research.

Research Laboratory,
Tokyo Electric Co.,
Kawasaki, Kanagawaken,
Japan.

Plate I

Fig. 1

×8

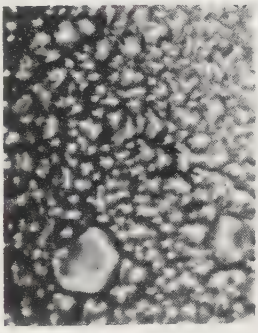
Fig. 2

×8

Fig. 4

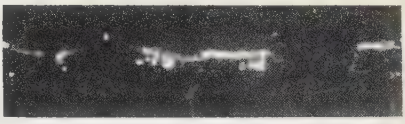
×26

Fig. 5



×650

Fig. 3



×10

Fig. 8

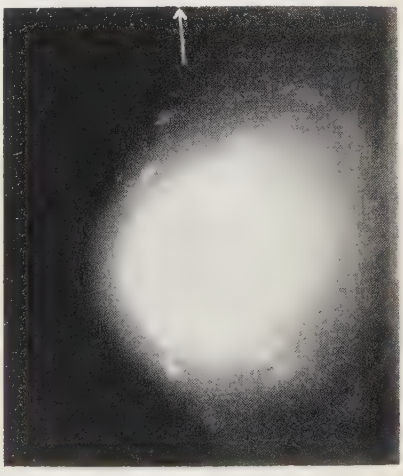


Fig. 7

×650

Fig. 6

×26

Fig. 9

Fig. 10

Effects of the Direction of Drawing on the Arrangement of the Micro-crystals in Aluminium Wire and on its Tensile Strength and Broken Fracture

By

Takeo Fujiwara

(Received November 20, 1931)

Abstract

By means of micro- and Laue-photographs the effect of the direction of drawing on the arrangement of the micro-crystals in drawn wire of aluminium was examined; and the effects on the tensile strength and on the broken fracture were also studied by an ordinary tensile testing machine and micro-photographs and radiographs.

In the exterior part of the wire drawn always in the same direction, the micro-crystals, whose crystallographic [111] axes are inclined to the direction of the drawing towards the exterior side and lie on a cone, were most predominant. In the wire drawn in reverse directions alternately, the micro-crystals were so arranged in the exterior part, that the [111] axes were inclined to the axis of the wire on both sides, interior and exterior, and the amount of their angular displacements was less than that of the one drawn always in the same direction. In both wires, the inclination of the [111] axis stated above became smaller as the core of the wire was approached, and it also became smaller with the increased reduction in diameter caused by successive drawing. The change in the arrangement of the micro-crystals was marked in the cases of 87% to 89% reductions in diameter and it diminished with further reduction, and in the wires reduced by about 94% in diameter hardly any change could be recognised in the radiographs.

The wire drawn in the same direction was more hardened and brittle than that drawn in reverse directions alternately and the tensile strength and the broken fracture differed in both cases though the difference was small in the former case.

Introduction

Many investigators have already ascertained that the direction of the axis of the fibrous arrangement of micro-crystals in hard drawn wire is nearly parallel to the axis of the wire, and that in the face-

centred lattice form its crystallographic directions are [111] and [100][1]. Some years ago, I suggested that in aluminium wire the [111] directions are not strictly parallel to the axis of the wire but lie in a cone with a small vertex angle about this axis.[2] Since then, this subject has been studied in other metals (Cu, Au, Ag, Ni) by many investigators.[3]

In the present experiment, I have examined the effect of the direction of drawing on the arrangement of the micro-crystals in aluminium wires by means of Laue-photographs, and the effects on the tensile strength and on the broken fracture of it were also studied by means of an ordinary tensile testing machine and micro-photographs and radiographs.

Experimental Method and Results

1. Materials

The experiment was, in most cases, carried out with aluminium circular wires of 0.3 to 0.9 mms. in diameter, which were prepared by drawing one part of a rod of about 5 mms. in diameter, through metallic dies successively always in the same direction, and also by drawing the other part in reverse directions alternately. Previous to cutting the rod into two parts it was annealed uniformly, and the dies and the drawing speeds etc. used in preparing the two kinds of wires were exactly the same.

2. X-Ray Examination of the Fibrous Arrangement

At each stage of the drawing of the two kinds of aluminium wires, the Laue-photographs were taken with the whole wire or with a definite part of it, by sending a narrow and circular beam of X-rays, which started from the focus on the Mo-target of a Coolidge

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1. M. Ettisch, M. Polanyi & K. Weissenberg: Zeit. f. Phys., **7**, 181 (1921), Zeit. Phys. Chem., **99**, 322 (1921).
   A. Ono: Memoirs Coll. Eng. Kyushu, **2** (1922)
   G. Sachs & E. Schiebold: Zeit. f. Metallk, **17**, 400 (1925).
2. T. Fujiwara: These Memoirs, **8**, 339 (1925).
3. E. Schmid & G. Wessermann: Zeit. f. Phys., **42**, 779 (1927).
   S. Takeyama: These Memoirs, **12**, 259 (1929).
   G. Greenwood: Zeit. f. Krist., **72**, 309 (1929).
   W. E. Remmers: Trans. A. I. M. E., p. 106 (1930).
   R. W. Drier and C. T. Eddy: Trans. A. I. M. E., p. 140 (1930).

tube, perpendicularly to the axis of the wire, The portions of the wire to be examined were prepared by removing enough of the outer layer of the wire to leave the proper thickness, by dissolving it in hydrochloric acid. The arrangement of the micro-crystals in these specimens was determined by treating their X-ray radiographs thus taken with the crystallographic globe devised by Prof. U. Yoshida, Kyoto Imperial University[1], and some effect of the direction of drawing on the fibrous arrangement of the micro-crystals in the aluminium wire could be detected. Some of the Laue-photographs thus taken are shown in Plates I and II.

3. Tensile Strength and Fracture of Broken Edge

The tensile strength of the aluminium wires was measured, at each stage of drawing, by the usual testing method with an ordinary tensile testing machine. The tensile strength, in Kg. per mm.,^{2} obtained for various sizes, is tabulated in Table I, where the value of the

Table I

Diameter of wire in mm.		2.17	1.67	1.28	1.00	0.79	0.64	0.60	0.54	0.43	0.34
Tensile strength in kg./mm.^{2}	Same direction.	13.8	17.3	18.3	22.2	24.4	28.6	32.8	32.6	36.7	39.3
	Reverse direction.	14.0	17.2	18.9	21.4	24.3	28.6	29.5	31.8	35.5	36.5

wires drawn always in the same direction and that of the wires drawn in reverse directions alternately are given in the 2nd and 3rd horizontal rows respectively.

The tensile strength of the wire drawn in the same direction was, as is seen in Table I, a little greater than that of the wire drawn in reverse directions for wires smaller than 0.6 mms. in diameter.

The fracture of the broken edge was then studied by means of micro-photographs. It was found that all of the wires drawn in reverse directions alternately were broken with the fractures shown in Fig. 8 in Plate I, and that those drawn always in the same direction were broken into two kinds of fractures as shown in Figs. 7 & 8 in Plate I, and many fractures of the kind shown in Fig. 7, Plate I, appeared

1. U. Yoshida: Japanese, J. Phys., **4**, 133 (1927);
S. Takeyama: These Memoirs, **12**, 257 (1929).

in wires of 0.64–0.54 mms. in diameter. In Table II the number of broken fractures of the kind shown in Fig. 7, Plate I, at different stages of drawing, is tabulated in percentage against that of the fractures shown in Fig. 8, Plate I.

Table II

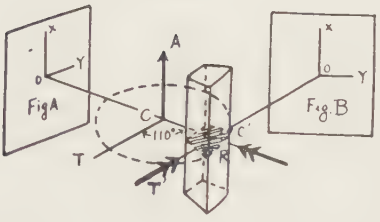
Diameter of wire in mm.		1.00	0.79	0.64	0.60	0.54	0.43	0.34
Number of Fractures of the kind shown in Fig. 7, Plate I, in %.	Same direction.	0	0	85	80	70	65	40
	Reverse direction.	0	0	0	10	0	0	0

Discussion of the Results

The Laue-photographs taken in the present experiment were nearly the same as those already obtained by me,[1] but those taken with wires 0.5–0.9 mms. in diameter, drawn always in the same direction through a certain numbers of dies, differed from the former ones, and the change in the X-ray radiographs taken with the wires drawn always in the same direction and in those drawn in reverse directions alternately appeared clearly, as may be seen in Figs. 1, 2, 3, 4, 5 and 6 in Plate I. Figs. 1, 3 & 5 Plate I, are the diffraction patterns obtained with wires of 0.54 mm. in diameter drawn in the same direction and Figs. 2, 4 and 6, Plate I, are those with wires of the same size drawn in reverse directions alternately. In these patterns Figs. 1 and 2, Plate I, were taken with circular wires by sending a beam of X-rays, which covered all parts of the cross section of the wire, perpendicularly to the axis of the wire; and Figs. 3, 4, 5 & 6 were taken with definite parts of the wires as shown in Fig. 1, where Fig. A corresponds to Figs. 3 and 4, Plate I and Fig. B corresponds to Figs. 5 & 6 Plate I, respectively. In Fig. 1 the plane RCT is a cross section perpendicular to the axis of the wire, the shadowed part is a portion illuminated by X-rays, RC the radial direction, CA the axis of the wire, CT the direction inclined at an angle of about 110° to the radial direction CR, C'T' is parallel to CT and the lines provided with two arrows indicate the directions of the incident X-rays respectively.

1. T. Fujiwara: loc. cit.

Fig. 1



The clear difference which can be recognised between these Laue-photographs taken with two different kind of wires, is that in all the radiographs in Figs. 2, 4 & 6, Plate I taken with the wire drawn in reverse directions alternately, the bands and spots are distributed symmetrically to the lines OX and OY, but in the radiographs taken with the wires drawn in the same direction they are distributed symmetrically only to the vertical line OX, except in Fig. 5, Plate I. In Fig. 5, Plate I, the bands and spots are distributed unsymmetrically to both the lines OX and OY and the radiating band due to the atomic plane (111), which appeared in the direction OX, parallel to the axis of the wire in Fig. 6 of Plate I, which was taken with the wire drawn in the reverse way, appears in the direction making an angle of about 20° to OX. The change in the diffraction patterns stated above was marked in wires, 0.54 mm. in diameter, reduced 89% in diameter, and with further reduction in diameter by further drawing it diminished and in wires thinner than 0.30 mm. in diameter the change could hardly be recognised in the radiographs.

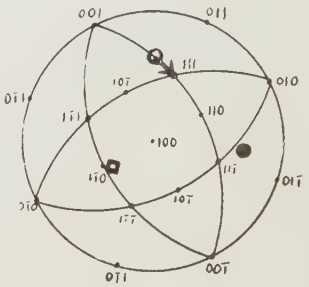
In the wires of the same size the change mentioned above was marked in the exterior layer and was hardly recognised in the interior layer, as is shown in Figs. 1, 2, 3 and 4 in Plate II. Figs. 1 & 2, Plate II are the diffraction patterns taken with wires 0.64 mm. in diameter. The radiographs shown in Figs. 3 and 4 in Plate II were taken with the same wire, etched to a diameter of 0.25 mm.

From Figs. 1, 3 and 5, Plate I, taken with a definite portion of the wire, it was found that in the exterior part of the wire drawn always in the same direction the micro-crystals, whose crystallographic [111] axes are inclined to the direction of the drawing towards one side as shown in Fig. 2 in stereographic projection, are most predominant. In Fig. 2, where an extreme orientation of the crystal is represented, the points marked ○, ● and □ respectively indicate the direction of the drawing, the radial direction and the direction of the beam of incident X-rays, and the arrow shows the direction of the angular displacement of the crystallographic [111] axis from the axis of the wire. In the case of the wire drawn in reverse directions alternately, the micro-crystals are so arranged in the exterior part

that the [111] axes are inclined to the axis of the wire on both sides and the amount of their angular displacements is less than that of the wire drawn in the same way.

It was also found that the inclination of the [111] axis became smaller as the core of the wire was approached and in the core of both wires, 0.64 mm. in diameter, prepared by two different kinds of drawings, a double structure was found though the number of micro-crystals arranged with the [100] direction parallel to the fibre axis was small. One of the typical Laue-photographs is shown in Fig. 5, Plate II, which was taken with the same wire as that which gave rise to Fig. 1, Plate II, after it had been etched to a diameter of 0.13 mm. The inclination of the [111] axis became smaller with the increased reduction in diameter caused by successive drawings; and in hard-drawn wire, 0.11 mm. in diameter, the structure was one in which the [111] direction was nearly parallel to the fibre axis or the direction of drawing. Fig. 6 in Plate II, is a Laue-photograph taken with wire of 0.11 mm. in diameter, drawn always in the same direction.

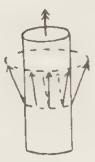
Fig. 2



Now in a circular drawn wire, as has already been suggested, the preferred orientation of the micro-crystals seems to change gradually from the surface of the wire to its core; therefore the [111] axis mentioned above is arranged in a conical manner and the vertex angle of the cone is larger in the exterior layer than in the interior, as is represented diagrammatically in Figs. 3 and 4. Figs. 3 and 4 represent the arrangements of the trigonal axis in the outer layer of the wire drawn in the same direction and in reverse directions respectively, and in these diagrams the lines provided with two arrows indicate the direction of drawing and the lines provided with one arrow the [111] axis. But strictly speaking the [111] axis slightly deviated from the generating line of the cone mentioned above as is shown in Fig. 3, where the dotted lines indicate the deviated position of the [111] axis.

When such a wire, in which the micro-crystals are arranged as shown in Figs. 3 and 4, is illuminated by X-rays, then the spots and bands appearing on the photograph in a certain direction will be mostly caused by the atomic planes of the crystals situated at a

Fig. 3. Fig. 4



definite position in reference to the direction of the incident X-rays; and thus the diffraction patterns due to the atomic (111) planes will become as shown in Figs. 5, 6 & 7. These are the typical figures calculated from the above considerations, Figs. 5 & 6 being the case of the wire drawn always in the same direction, and Fig. 7 that of the wire drawn in reverse directions alternately. In these diagrams the shadowed parts indicate the part of the cross section of the wire which is illuminated by the X-rays, and the curved lines *a*, *b*, *c* and *d* indicate the positions of the diffraction spots caused by the atomic (111) planes of the crystals situated at the positions, A, B, C and D respectively. The lines provided with two arrows and one arrow indicate respectively the direction of the illuminating X-rays and the direction of drawing. The correctness of the considerations above stated will be seen from the agreement of the diagrams thus calculated with the Laue-photographs actually taken. Fig. 7, Plate II, corresponds to the calculated diagram shown in Fig. 5; Fig. 1, Plate I and Fig. 1 Plate II to Fig. 6 and Fig. 2, Plate I, and Figs. 2 & 8, Plate II, to Fig. 7. A fine structure of the lines *a*, *b*, *c* and *d* in the calculated diagrams is seen clearly in these Laue-photographs.

It is well known that when a crystal aggregate in a wire is subjected to a drawing process each grain which has a certain preferred orientation is deformed by two different kinds of forces, extension in the direction nearly parallel to the direction of drawing and compression parallel to the radial direction of the wire. This deformation is usually considered to take place by slipping on certain appropriate atomic planes, causing the micro-crystals to take a definite orientation with respect to the direction of force. Though the exact mechanism of the deformation of the crystals in the wire produced by drawing is not yet clear, but the foregoing orientation of the micro-crystals in a drawn wire of aluminium seems to be explainable, at least to some extent, by a combination of the results already obtained by others in the cases of extension[1] and compression.[2]

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1. G. I. Taylor and G. F. Flam: Proc. Roy. Soc., **102**, 643 (1923).
   K. Fujii: These Memoirs, **13**, 101 (1930).
2. S. Tsuboi: These Memoirs, **11**, 375 (1928).
   Y. Fukami: These Memoirs, **12**, 261 (1929).

It has already been stated that some differences in the tensile strength and the broken fracture could be detected with two kinds of the wires prepared by drawing in different manners. Some differences between the two kinds of the wires can also be observed in the breaking marks caused on the surface of the wires by bending, as is shown by the micro-photographs reproduced in Figs. 9 and 10 of Plate II. Fig. 9 corresponds to the wire drawn in the same direction, and Fig. 10 to the wire drawn in reverse directions alternately. The

Fig. 5

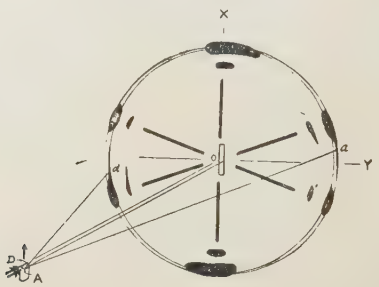


Fig. 6

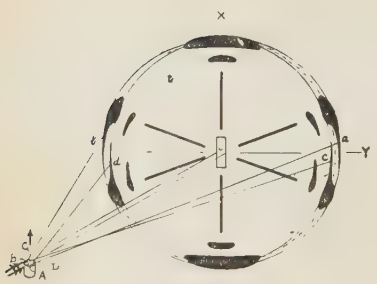
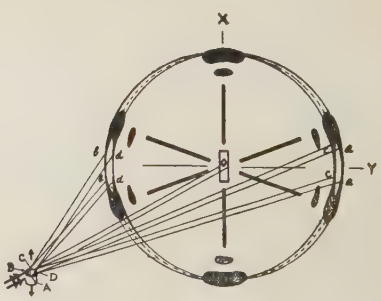


Fig. 7



diameter of the wire is 0.54 mm. in both cases. It seems to be possible to say clearly now, from the present investigation, that the differences in the properties of the two kinds of the wires as above stated are due, though not wholly, to the difference in the arrangement of the micro-crystals in the two kinds of the wires, as was stated before.

In conclusion, I wish to express my sincere thanks to Prof. U. Yoshida, of the Kyoto Imperial University for the interest he has taken in this research.

Research Laboratory,
Tokyo Electric Co.,
Kawasaki, Kanagawaken,
Japan.

Plate I

(The arrow indicates the direction of drawing)

Fig. 1

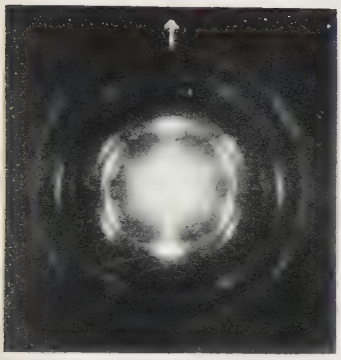


Fig. 3

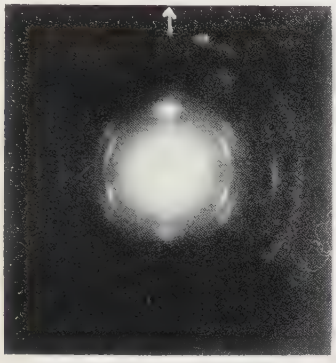


Fig. 5

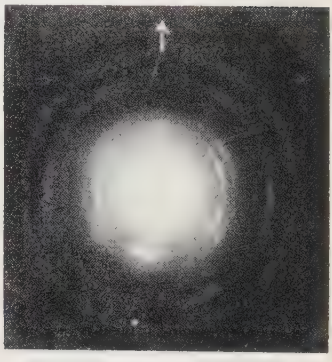


Fig. 2

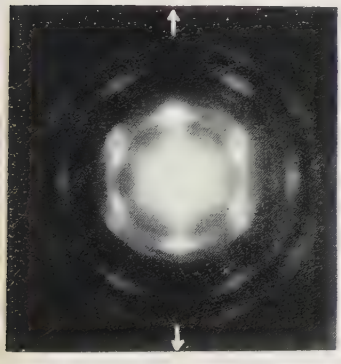


Fig. 4

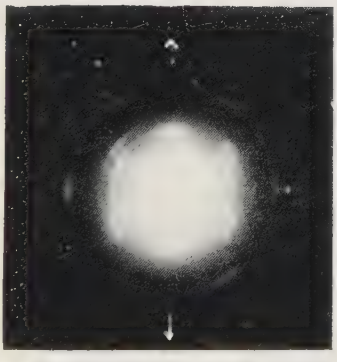


Fig. 6

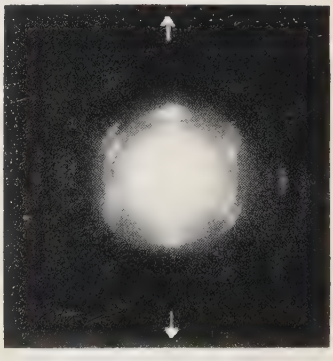


Fig. 7

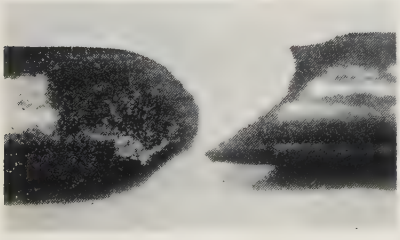


Fig. 8

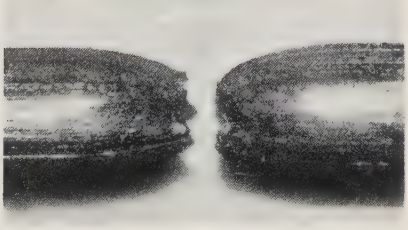


Plate II

(The arrow indicates the direction of drawing)

Fig. 1

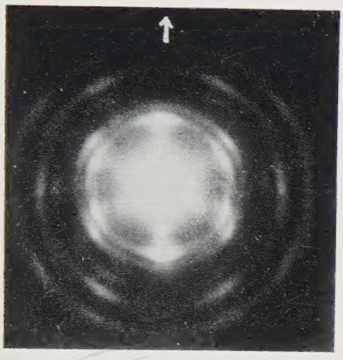


Fig. 3

Fig. 5

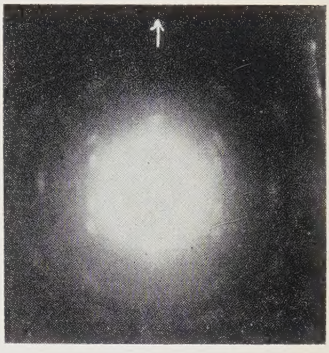


Fig. 2

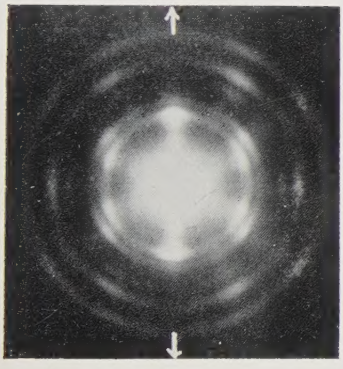


Fig. 4

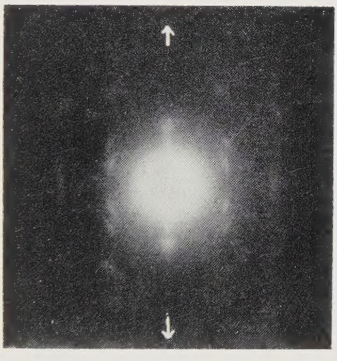


Fig. 6

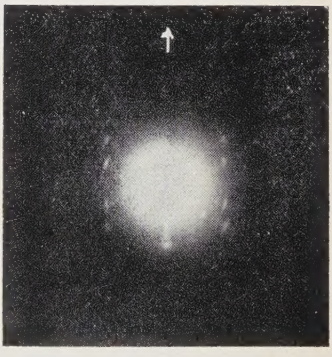


Fig. 7

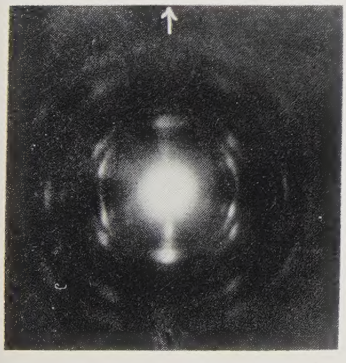


Fig. 8

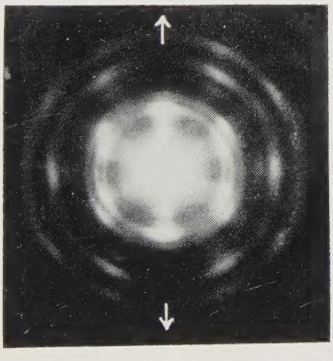


Fig. 9

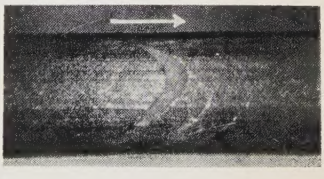
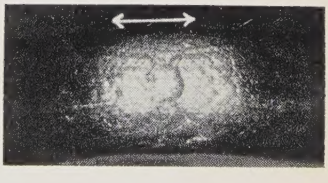


Fig. 10



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